Heavy metals availability for plants in a mining area from North-Western Romania

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1. Abstract

An important concern for human health is the uptake of contaminants by plants from soil and their consumption by humans. The concentrations of heavy metals (lead, copper, cadmium) in the soil and plant samples collected from a village near sedimentation ponds, north-western Romania have been determined by inductively coupled plasma atomic emission spectrometry after *aqua regia* digestion and by inductively coupled mass spectrometry after water extraction for soil, and acid microwave digestion for plants. Plant uptake factors were calculated for home grown vegetables (tomatoes, carrots) in this area. Correlation analysis identified a strong relationship between metals concentrations in soil and vegetables. The results of this study revealed that the consumption of vegetables grown in the vicinity of industrial areas pose a significant health risk to humans.

2. Introduction

As a result of increasing anthropogenic activities, the heavy metal pollution of soil, water, and atmosphere represents a growing environmental problem affecting food quality and human health. Heavy metals may enter the food chain as a result of their uptake by edible plants, thus, the determination of heavy metals in environmental samples is very important [Alirzaveya et al. (2006), Kachenko et al. (2004)].

The interactions between metals and solid phases of soil, soil water, and air within and above soil depends of a variety of chemical factors and determine the heavy metal transport and fate. Absorption of metals from soil water to soil particles is the most important chemical determinant that limits mobility in soils [Curtis et al. (2002)]. Heavy metals from soil enter plants primarily through the root system. In general, plant roots are the most important site for uptake chemicals from soil [Bell (1992)].

Heavy metals may have significantly toxic and hazardous effects on human health, especially cadmium and lead, as non-essential elements [Bakirdere et al. (2008)].

Cadmium tends to be very mobile in soil systems and therefore very available to plants. Cd^{2+} is the main species in soil solution. Accumulation of cadmium in food crops at soil concentrations that are not phytotoxic is a significant concern. Plant species differ widely in their tendency to accumulate cadmium. Absorption/desorption of cadmium is about 10-fold more rapid than that of lead. Chronic cadmium exposures result in kidney damage, bone deformities, and cardiovascular problems [Curtis et al. (2002), Fritioff et al. (2007)].

Lead is especially accumulated in surface horizon of soil because its low water solubility within an environmentally relevant pH range results in very low mobility. Neurological problems, especially in children, are the principal concern for chronic lead exposure, along with other health-endangering effects, such as blood enzyme changes, anemia and hyperactivity [Curtis et al. (2002), Barkirdere et al. (2008)].

It is known that copper is an essential element, but it may be toxic to both human and animals when its concentration exceeds the safe limits and its concentration in some human tissues such as thyroid can be changed dependent on the tissue state providing even cancerous or non-cancerous effects [Bakirdere et al. (2008), Yaman et al. (2005)].

The primary concern with the uptake of contaminants by plants is the presence of contaminants in produce consumed by humans.

This paper reports the determination of heavy metals in soil and vegetables samples for the pollution assessment of the residential properties located in a rural area, in the vicinity of Baia Mare, North-Western Romania.

2.1. Study area

In the Baia Mare area, around an industrial complex involved in mining, metallurgical and chemical activities, the environment and particularly the soils are polluted due to the acid rains and heavy metal emissions [Lacatusu et al. (2001)].

The investigated rural area is situated near three sedimentation ponds. The strong winds from the sedimentation ponds area displace fine particulates, containing heavy metals, from ponds' walls and deposited in adjacent area, contaminating the air, soil and vegetation. Also, residual water infiltration from the sedimentation pond with high heavy metal contents has a serious contribution to the pollutant dispersion in soil and ground waters, reaching also the food chain, since the residents from rural adjacent areas cultivate the vegetables and the animals feed in their own gardens. Considering all these aspects, it is important to monitor the heavy metal pollution in soils from this area [Mihaly-Cozmuta et al. (2005), Cordos et al. (2006)] .The sampling sites of soils are represented in Figure 1.

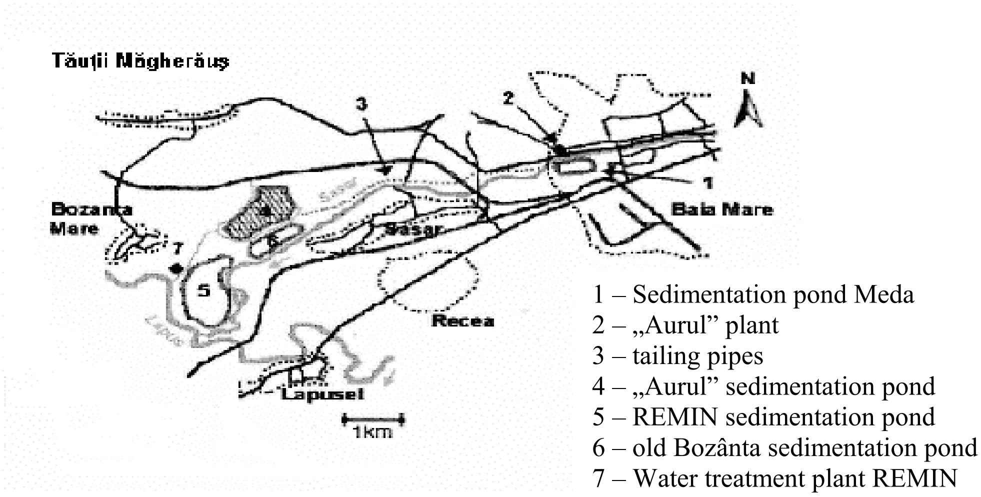

Figure 1 The sampling sites of soils

3. Methods

A number of 15 soil and 15 plant samples were collected in the rural area, in March 2006, from the gardens belonging to the houses in the vicinity of sedimentation ponds. Soil was collected in the root zone of vegetable sample. Thus, soil and vegetable are complementarily sampled.

3.1 Soil samples

Soil samples were collected at 0-20 cm depth and stored in polyethylene bags for transport to laboratory. The soil samples were air-dried, mechanically ground and sieved. To determine the total metal content, fraction below 2 mm was digested in *aqua regia* (HCl 37.5% and HNO_3 65%), during 16 hours at room temperature and then, 2 hours, at reflux conditions. The extract was analyzed by inductively coupled plasma atomic emission spectrometer (ICP-AES) using a SPECTRO FLAME (SPECTRO, Kleve, Germany).

To determine the water soluble heavy metal contents, soil samples were extracted in distilled water, during 1 hour at room temperature. Because the heavy metal concentration extracted in distilled water were below ICP-AES detection limits, the analysis of metals content was performed using inductively coupled plasma mass spectrometry, ICP-MS ELAN DRC II (Perkin Elmer, USA), due to its excellent detection limits.

3.2 Plant samples

The plant samples were washed in distilled water, dried at 105 °C for 24 h and grounded to obtain a homogenized powder. The samples were then digested in HNO_3:$HClO_4$ (7:3, v/v). Metals concentrations were measured using ICP-MS. The quantification was performed using an external calibration with multielemental Merck standard solution.

All chemicals used were of high-purity reagent grade. Throughout all analytical work, ultrapure water (Millipore, 18.2 MΩ/cm) was used. The detection limits and the uncertainties of the methods used in ICP-AES and ICP-MS analyses are given in Table 1.

4. Results

The obtained results showed that in soil, the concentration of Pb ranged between 108 and 397 mg/kg, with an average value of 268 mg/kg. The concentration of Cu was between 66.3 and 238.1 mg/kg, with an average of 123.5 mg/kg and the Cd concentration between 0.48 and 3.12 mg/kg, with an average of 1.87 mg/kg. All Pb values exceeded intervention level (100 mg/kg), 60% of Cu concentrations exceeded alert level (100 mg/kg) and 20% of Cd concentrations exceeded alert level (3 mg/kg), for sensitive soils, according to Romanian legislation.

Lead, Cu and Cd concentrations in vegetables sampled had a similar trend to soil heavy metals concentrations. Lead levels ranged from 0.26 to 3.24 mg/kg dry weight in tomatoes and from 0.50 to 3.10 mg/kg in carrots, with mean of values 2.00 and 1.61 mg/kg, respectively. Copper concentrations were between 3.42 and 15.01 mg/kg in tomatoes and between 2.64 and 19.55 in carrots with an average values of 7.60 and 8.55 mg/kg, respectively. Cadmium concentrations varied between 0.21 and 4.21 mg/kg in tomatoes and between 0.09 and 3.56 mg/kg in carrots, with mean values of 1.37 and 0.83 mg/kg, respectively.

In all vegetables samples lead and cadmium concentrations are above maximum levels (except Cd level for one carrot sample). The obtained concentrations were compared to maximum levels of lead (0.20 mg/kg in both vegetables) and cadmium (0.10 mg/kg in carrots and 0.050 mg/kg in tomatoes) according to European Commission Regulation (EC) No 1881/2006.

Table 1 The detection limits and the uncertainties of the methods used in ICP-AES and ICP-MS analyses

	ICP AES		ICP-MS	
Element	Detection limit, mg/kg	Uncertainty, %	Detection limit, mg/kg	Uncertainty, %
Pb	2.2	8.9	0.10	6.8
Cu	0.25	7.9	0.22	7.4
Cd	0.25	9.2	0.055	6.2
Zn	0.5	7.8	0.86	6.2

The correlation coefficients between metals concentrations in soil and vegetables are shown in Tables 2, 3 and 4.

Significant correlation was observed between soluble lead from soil and lead in carrots and high correlations between Pb from tomatoes and carrots and Pb in soil extractable *in aqua regia*, lead in tomatoes and carrots, and the same for Cd and Cu concentrations. Also, high correlations were revealed between soluble Cu and extractable with *aqua regia* in soil, and between Cu in carrots and tomatoes. These findings suggest interaction between Pb, Cu, Cd in both vegetables and soil are important, in relation to the known geochemical association between the studied three metals. The soil metal concentrations appear to influence the uptake of Pb, Cu, Cd in vegetables [Kachenko et al. (2004)].

Table 2 Correlation coefficients between Pb concentrations in soils and vegetables

	Pb T	Pb M	Pb tomato	Pb carrot
Pb T	1.000	0.461	0.883**	0.905**
Pb M		1.000	0.365	0.590*
Pb tomato			1.000	0.750**
Pb carrot				1.000

* significant at p<0,05; ** significant at p<0,01

T – refers to metals extractable in *aqua regia*;

M- referts to metals extractable in distilled water

Table 3 Correlation coefficients between Cd concentrations in soils and vegetables

	Cd T	Cd M	Cd tomato	Cd carrot
Cd T	1.000	-0.175	0.959**	0.782**
Cd M		1.000	-0.147	-0.049
Cd tomato			1.000	0.885**
Cd carrot				1.000

* significant at p<0,05; ** significant at p<0,01

Table 4 Correlation coefficients between Cu concentrations in soils and vegetables

	Cu T	Cu M	Cu tomato	Cu carrot
Cu T	1.000	0.700**	0.843**	0.930**
Cu M		1.000	0.460	0.694**
Cu tomato			1.000	0.728**
Cu carrot				1.000

* significant at p<0,05; ** significant at p<0,01

The relationship between contaminant concentrations in soil and edible plant material is highly specific to the plant species. The relationship between contaminant concentration in edible produce and the concentration in soil is described using Plant Uptake Factor (PUF), which is defined as follows:

PUF = Concentration in edible portion of plant (mg/kg) / Concentration in soil (mg/kg)

The PUF values quantify the relative differences in bioavailability of metals to plants and identify the efficiency of a plant species to accumulate a given metal. The PUFs as suggested by Kloke *et al*. (1984) for Cu and Pb (0.01-01), and Cd (1-10) were used as a generalized range for comparison. These factors were based on the root uptake of metals and surface absorption of atmospheric metal deposits [Kachenko et al. (2004)].

The obtained values for PUF are shown in Table 5 and no sample exceeded the values indicated by Kloke *et al*.

Table 5 The average PUFs values for the vegetables in the rural area

Element	Tomatoes	Carrots
Pb	0.0072	0.0058
Cd	0.0622	0.0649
Cu	0.6703	0.4120

This study highlights that heavy metals contamination of soils and vegetables in rural area, near Baia Mare is significant, indicating a severe situation, needing urgent measurements of pollution stopping and applying soil decontamination solutions, especially they cannot be degraded or destroyed.

Due to the high heavy metal content in the studied area the metal accumulation in vegetables grown in the vicinity of industrial sites represents a potential risk for public health.

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